

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

REVISED VERSION

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
29 April 2004 (29.04.2004)

PCT

(10) International Publication Number
WO 2004/035200 A3

(51) International Patent Classification⁷: **B01J 21/12,**
23/46, 23/42, 29/86, 29/85

BUSCA, Guido [IT/IT]; Plaza G.Martinez 5/11, I-16133 GENOVA (IT). **JIMENEZ-LOPEZ, Antonio** [ES/ES]; Calle Camino de Ronda 115, 6ºA, GRENADE (ES). **RODRIGUEZ-CASTELLON, Enrique** [ES/ES]; Calle Pajarete 5, Alhaurin de la Torre, 29130 MALAGA (ES). **MAIRELES-TORRES, Pedro** [ES/ES]; Plaza Castillejos, Bloque 4-1ºD, 29009 MALAGA (ES).

(21) International Application Number:
PCT/EP2003/014857

(74) Agents: **COLOMBET, Alain et al.**; CABINET LAVOIX, 2, place d'Estienne d'Orves, F-75441 PARIS CEDEX 09 (FR).

(22) International Filing Date: 15 October 2003 (15.10.2003)

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(26) Publication Language: English

Published:

— with international search report

(88) Date of publication of the international search report: 7 October 2004
Date of publication of the revised international search report: 2 December 2004

(30) Priority Data:
02356201.0 15 October 2002 (15.10.2002) EP

(71) Applicants (for all designated States except US): CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (C.N.R.S) [FR/FR]; 3, rue Michel Ange, F-75016 PARIS (FR). UNIVERSITE DE MONTPELLIER II [FR/FR]; Place E. Bataillon, F-34095 MONTPELLIER CEDEX 05 (FR). SNAMPROGETTI S.P.A. [IT/IT]; Viale de Gaspari, 16, I-20097 SAN DONATO MILANESE (IT). CONSORZIO INTERUNIVERSITARIO NAZIONALE PER LA SCIENZA E TECHNOLOGIA DEI MATERIALI [IT/IT]; Via Benedetto Varchi, I-50132 FIRENZE (IT). REPSOL YPF S.A. [ES/ES]; Pº de la Castellana 278, E-28046 Madrid (ES).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **TREJO-MENAYO, José-Manuel** [ES/ES]; Rafaela Bonilla, 21, 6º C, E-28028 Madrid (ES). **ROZIERE, Jacques** [FR/FR]; Les Chênes Colombières, BT J2, 58, avenue d'Occitanie, F-34090 MONTPELLIER (FR). **JONES, Deborah** [GB/FR]; Les Chênes Colombières, BT J2, 58, avenue d'Occitanie, F-34090 MONTPELLIER (FR). **JACQUIN, Mélanie** [FR/FR]; 145, rue de Salaison, F-34170 CASTELLAU-LE-LEZ (FR). **ROSSINI, Stefano** [IT/IT]; Via Duccio Arturo 10, I-20142 MILANO (IT). **CATANI, Roberto** [IT/IT]; Via San Venerio 5/d, I-20138 MILANO (IT). **VACCARI, Angelo** [IT/IT]; Via Belletini 16, I-40127 BOLOGNA (IT). **LENARDA, Maurizio** [IT/IT]; Calle Coni Zugna 16, S. Elena, I-30100 VENEZIA (IT).

(15) Information about Correction:
see PCT Gazette No. 49/2004 of 2 December 2004, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POROUS CATALYTIC SYSTEM FOR OLIGOMERISING LIGHT OLEFINS

(57)-Abstract: The present invention relates to the use of a silicon-based porous catalytic system for oligomerising light olefins said porous silicon-based catalytic system having an average pore diameter of between about 1 nm and about 5 nm and an acidity level of between about 150 µmol/g and about 650 µmol/g, and prepared from at least one hydrolysable silicon-based compound, or other source of silicon, and at least one non-ionic surface active agent. The invention also relates to a process for oligomerising light olefins using said silicon-based porous catalytic system, and to certain silicon-based porous catalytic systems.

WO 2004/035200 A3

INTERNATIONAL SEARCH REPORT

International Application No

PC 03/14857

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J21/12 B01J23/46 B01J23/42 B01J29/86 B01J29/85

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/131930 A1 (LIU YU ET AL) 19 September 2002 (2002-09-19) the whole document -----	1-11, 19-35, 43-47
Y	US 5 270 273 A (PELRINE BRUCE P ET AL) 14 December 1993 (1993-12-14) column 3, line 37 - column 17, line 10; claims; examples; tables -----	1-48
A	EP 0 272 496 A (ENIRICERCHE S.P.A.) 29 June 1988 (1988-06-29) the whole document -----	
Y	US 6 204 424 B1 (PUJARI AJIT ATMARAM ET AL) 20 March 2001 (2001-03-20) column 2, line 36 - column 5, line 20; claims; examples; tables ----- -/-	1-48

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 September 2004

Date of mailing of the international search report

25.09.04

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

de Cauwer, R

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 03/14857

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 299 855 B1 (CARRAZZA JOSE ET AL) 9 October 2001 (2001-10-09) column 2, line 53 - column 9, line 35; claims; examples; tables -----	20-24

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

1-48

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: Claims 1-11, 19-35 and 43-47 (in as far as they relate to a substantial catalytic metal-free porous system)

A porous silicon-based catalytic system substantially free from catalytic metal; The use of said catalytic system for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

2. claims: Claims 1-10, 12, 18, 19, 25-34, 36, 39 and 43-47 (in as far as they relate to a porous system containing catalytic metals chosen from groups 8,9 and 10)

The use of a porous silicon-based catalytic system containing one or more catalytic metals chosen from groups 8,9 and 10 for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

3. claims: Claims 1-10, 12-15, 17-19, 25-34, 36-39, 41 and 43-47 (in as far as they relate to a porous system containing only platinum as catalytic metal)

The use of a porous silicon-based catalytic system containing platinum for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

4. claims: Claims 1-10, 12-16, 18-19, 25-34, 36-40 and 43-47 (in as far as they relate to a porous system containing only rhodium as catalytic metal)

The use of a porous silicon-based catalytic system containing rhodium for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

5. claims: Claims 1-10, 12-15, 18-19, 25-34, 36-39 and 42-47 (in as

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

far as they relate to a porous system
containing platinum and
rhodium as catalytic metal)

The use of a porous silicon-based catalytic system
containing platinum AND rhodium for converting a light
olefin feedstock into oligomer paraffins, and a process
for converting a light olefin feedstock into oligomer
paraffins using
said catalytic system

6. claim: Claim 48

Diesel fractions

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/14857

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2002131930	A1	19-09-2002	US	6585952 B1		01-07-2003
			US	2002018747 A1		14-02-2002
			WO	03053849 A1		03-07-2003
			AU	5297601 A		11-12-2001
			EP	1296894 A1		02-04-2003
			JP	2003535009 T		25-11-2003
			WO	0192154 A1		06-12-2001
			US	2002182143 A1		05-12-2002
			US	2002187098 A1		12-12-2002
			US	2002182144 A1		05-12-2002
			US	2004067842 A1		08-04-2004
US 5270273	A	14-12-1993	US	5105051 A		14-04-1992
EP 0272496	A	29-06-1988	IT	1213433 B		20-12-1989
			CA	1290495 C		08-10-1991
			DE	3765527 D1		15-11-1990
			DK	669387 A		24-06-1988
			EP	0272496 A1		29-06-1988
			JP	63168406 A		12-07-1988
			NO	875290 A ,B,		24-06-1988
			US	5003125 A		26-03-1991
US 6204424	B1	20-03-2001	DE	19857314 A1		03-02-2000
			GB	2332155 A ,B		16-06-1999
			JP	3486566 B2		13-01-2004
			JP	2000042416 A		15-02-2000
US 6299855	B1	09-10-2001	US	6106802 A		22-08-2000
			US	5840271 A		24-11-1998
			BR	9900580 A		04-01-2000
			DE	29924407 U1		27-02-2003
			DE	69907530 D1		12-06-2003
			DE	69907530 T2		18-03-2004
			EP	0935996 A2		18-08-1999
			JP	3306387 B2		24-07-2002
			JP	11278827 A		12-10-1999
			US	6485702 B1		26-11-2002
			ZA	9901258 A		18-08-1999
			DE	19704875 A1		14-08-1997
			FR	2744933 A1		22-08-1997
			GB	2309967 A ,B		13-08-1997
			GB	2341853 A ,B		29-03-2000
			JP	3139740 B2		05-03-2001
			JP	10007474 A		13-01-1998
			NL	1005203 C2		10-08-2000
			NL	1005203 A1		12-08-1997